

Thermal Decomposition Kinetics of Strontium Oxalate

^aF. A. AL-NEWAISER, ^aS. A. AL-THABAITI, ^aA. O. AL-YOUBI, ^aA. Y. OBAID, and ^bM. A. GABAL*

^aChemistry Department, Faculty of Science, King Abdul Aziz University, Jeddah, Saudi Arabia

^bChemistry Department, Faculty of Science, Benha University, Benha, Egypt
e-mail: mgabalabdo@yahoo.com

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The thermal decomposition behavior in air of $\text{SrC}_2\text{O}_4 \cdot 1.25\text{H}_2\text{O}$ was studied up to the formation of SrO using DTA-TG-DTG techniques. The decomposition proceeds through four well-defined steps. The first two steps are attributed to the dehydration of the salt, while the third and fourth ones are assigned to the decomposition of the anhydrous strontium oxalate into SrCO_3 and the decomposition of SrCO_3 to SrO, respectively. The exothermic DTA peak found at around 300°C is ascribed to the recrystallization of the anhydrous strontium oxalate. On the other hand, the endothermic DTA peak observed at 910°C can be attributed to the transition of orthorhombic-hexagonal phase of SrCO_3 . The kinetics of the thermal decomposition of anhydrous strontium oxalate and strontium carbonate, which are formed as stable intermediates, have been studied using non-isothermal TG technique. Analysis of kinetic data was carried out assuming various solid-state reaction models and applying three different computational methods. The data analysis according to the composite method showed that the anhydrous oxalate decomposition is best described by the two-dimensional diffusion-controlled mechanism (D_2), while the decomposition of strontium carbonate is best fitted by means of the three-dimensional phase boundary-controlled mechanism (R_3). The values of activation parameters obtained using different methods were compared and discussed.

Keywords: strontium oxalate, DTA-TG, decomposition, kinetics, mechanism

INTRODUCTION

Processes involving chemical transformations of solids play an important role in modern technology, as sophisticated and costly solids can be produced by reaction of other, precursory solids [1].

The preparation of strontium oxalate presents a part of the study of oxalate precursor employed in the synthesis of BiSCCO ceramic superconductors [2] usually prepared by the solid-state thermochemical reaction of Bi_2O_3 , SrCO_3 , CaCO_3 , and CuO .

Strontium oxalate exists in two different forms [3], the neutral strontium oxalate hydrate, $\text{SrC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, and the acid salt of strontium oxalate, $\text{SrC}_2\text{O}_4 \cdot 1/2\text{H}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$. Depending on the concentration of oxalic acid and ammonium oxalate as precipitating agents, both forms can be obtained. At ap-

propriate pH, the stoichiometric compound $\text{SrC}_2\text{O}_4 \cdot 1/2\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is formed. The extent of hydration depends on the preparation conditions while a part of the crystallization water was reported to be zeolitic [4].

The thermal decomposition of various forms of strontium oxalates was studied in different atmospheres [3] using differential scanning calorimetry (DSC) and thermogravimetry (TG) coupled with Fourier transform infrared spectroscopy (FT-IR) and mass spectroscopy (MS). The results showed that the anhydrous acid oxalate decomposition was accompanied with the release of H_2O , CO , CO_2 , and formic acid. The studies on the hydrated salts by Dollimore et al. [4] showed a correlation between their crystal structure and the dehydration mode, where the dehydration of the triclinic single crystal of $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

*The author to whom the correspondence should be addressed.

Present address: Chemistry Department, Faculty of Science, King Abdul Aziz University, Jeddah, KSA.